CONSTRAINING THE MEAN RESIDENCE TIME AND FLOWPATH OF GROUNDWATER THROUGH COAL SEAMS USING NOBLE GASES

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Abstract

Noble gases, specifically ^{4}He concentrations, can be a useful tool for determining the rates of groundwater recharge, subsurface residence times, and groundwater flowpaths, especially in difficult to model complex formations such as fractured aquifers. This thesis focused on developing an approach to determine the age of formation waters within coalbed methane (CBM) reservoirs in the Powder River Basin (PRB). Specifically, the work explored the difficulties and corrections required to use the ^{4}He in-growth method to determine the residence time of groundwater in the fractured coal seams in this area. Coal seams are considered the primary aquifer of the PRB with groundwater being recharged by water from the west and flowing toward the basin center. Using the noble gas geochemistry of coal seam solids to conduct experimental work to determine the diffusional rates of ^{4}He from coal seam solids using step-heating experiments and bulk releases I was able to determine the ^{4}He accumulation rates in coal seams from the PRB. I then compared the data to produced formation waters and free gas samples, in combination with numerical modeling approaches, to develop an approach for determining the residence times of formation waters in this area. The results of this work provide important insights on the flowpaths along which groundwater recharges into the PRB.

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1. Introduction

Biogenic methane is produced through microbial metabolism of CO_2 or acetate by anaerobic respiration (Barnhart et al., 2016). Biogenic methane generation is the final step in the decay of organic matter, where electron acceptors such as oxygen become depleted, while carbon dioxide and hydrocarbon gases accumulate (Barnhart et al., 2016). Such production occurs in reducing, water saturated formations that are rich in organic matter. For these reasons, the Tongue River Formation in the Powder River Basin (PRB) is an example of an area where biogenic methane production is feasible (Wheaton and Metesh, 2002). As a result, across the PRB, the majority of coalbed methane is thought to be microbial or biogenic in origin (DOE, 2007; Flores et al., 2008).

Although the PRB has rich deposits of biogenic gas in coal seams throughout the basins, the extraction of microbial gas in this region, like many others, requires dewatering millions of gallons of water to lower the water table sufficiently for energy production. In the Powder River Basin in southeastern Montana, ~64 kiloliters of groundwater were extracted per day per well from 1993 to 2006 to produce coalbed methane (CBM), which in some cases led to severe declines in the water table (up to 190 m; Clarey et al., 2010). Conversely, the generation of biogenic methane is thought to be inextricably linked to the recharge of fresh water (Le Salle et al., 2001; Hagedorn, 2015; Vengosh et al., 2014). Thus, it is critical to understand groundwater dynamics in this and other CBM regions to evaluate biogenic methane formation and to evaluate the impacts of obtaining and producing it on groundwater supply and quality (Jones et al., 2013). The main natural gas-producing coal members present in this study area include the Knobloch, Terret, Nance, and Flowers-Goodale coal beds. This study seeks to use noble gas geochemistry to develop an understanding of groundwater dynamics in the PRB, particularly as the groundwater flowpaths

relate to the residence times of fluids in various formations (Le Salle et al., 2001; Wei et al., 2014; Hagedorn, 2015).

To approximate the residence time of groundwater, specifically in coalbed methane reservoirs is complex. Noble gas isotopic tracers can offer estimates of *in-situ* rates of microbial CBM production (Schlegel et al., 2011) and provide information about the timing and mechanisms of groundwater recharge and basin-scale fluid flow (Ge and Garven, 1992; Manning et al., 2005; Gurdak and Qi, 2006; Stute et al., 2007; Gupta et al., 2015). Determination of residence times of the groundwater faces many hurdles including the choice and reliability of tracers. While there are techniques and calculations established to overcome these potential anomalous results, there has been little research on mean residence times in coalbed aquifers (Cook et al., 1996; Darrah et al., 2015; Harkness et al., 2017; Sheldon et al., 2003).

2. Regional Geology

The Powder River Basin, location of the second largest coalbed natural gas play in the United States, is located in Wyoming and Montana (USGS, 2013). This study focuses on the groundwater residence times of fluids sourced from the Tongue River Member of the Fort Union Formation, located in the PRB of southeast Montana. The basin is an asymmetrical syncline with the deep axis (trending northwest to southeast) along the westernmost margin (Flores et al., 2008). The basin, which formed during the Laramide Orogeny, is bordered to the east by the Black Hills uplift, to the north by the Miles City Arch, to the south by the Laramide Mountains, and to the west by the Big Horn Uplift and Casper Arch (Anna, 2009). Throughout the Laramide Orogeny, the basin developed coal-forming mires between river systems bounded by the resulting uplift, in turn developing long-term drainage systems confined by domed mires where the Fort Union coal-beds accumulated (Flores and Ethridge 1985; Flores, 1986; Lillegraven, 1993; Flores, 2004).

3. Hydrogeology

The key to the generation of coalbed methane in the Fort Union Formation is the hydrogeology of the basin and coproduced water (Flores, 2004). In order to produce coalbed methane economically, the beds must be dewatered, allowing gas to desorb from the surfaces of coal, diffuse through its pores and cleats, exceed hydrostatic pressure, and flow to the natural-gas well (Wheaton and Metesh, 2002). Coal beds in the Fort Union Formation and various other formations throughout the PRB serve as important coalbed methane reservoirs, whose long lateral continuity and hydrologic communication creates a suitable environment for the production of coalbed methane. Without this continuity, there would be a lack of frequent inflow of nutrients and fresh water or outflow of bacterial waste products, which enables vital bacterial activity in the coal beds for methane generation. Beds that were discontinuous before reaching the outcrops did not receive this flow of water, and therefore failed to generate methane by bacterial activity. However, $^{87}Sr/^{86}Sr$ isotopes ranging between ~0.708 to ~0.712 ppm indicate that the groundwater from the sampling area is transported through the sandstone while intermittently flowing through the coal aquifer for shorter periods of time (Pearson, 2002; Campbell et al., 2008).

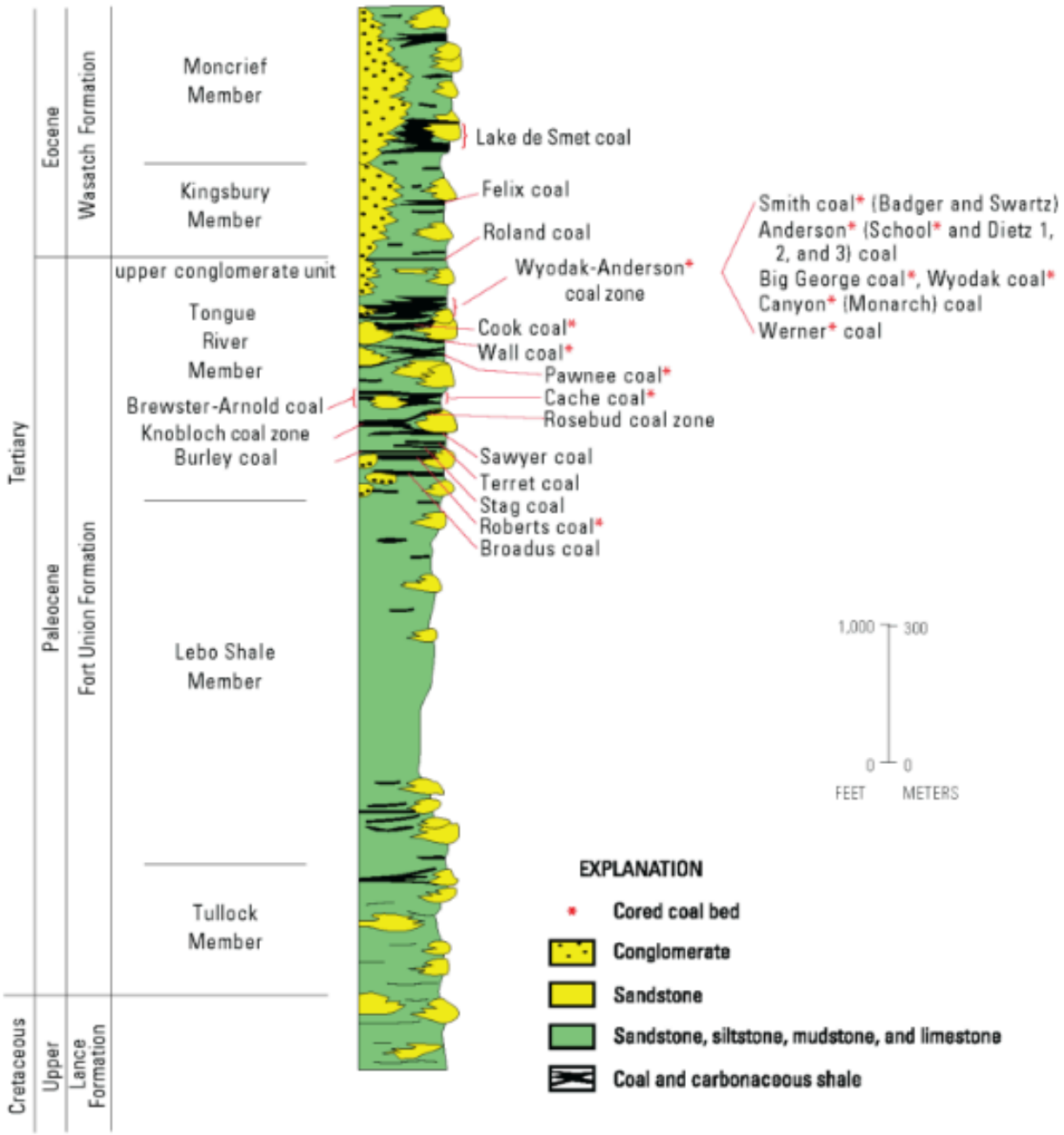

Figure 1 . General stratigraphy of the Fort Union Formation of the Powder River Basin (Flores, 2004).

4. Methodology

The water and gas samples reported in this study are taken from wells in the Flowers, Goodale, and Knobloch coal seams of the Fort Union Formation in the PRB of Wyoming, USA (Ritter et al., 2015). Samples from these wells were collected in May and July of 2014. The sample locations are depicted on the map in Figure 2. Well depth in the respective coal seams varied from 155 m to 528 m below ground surface. Samples were collected from seven coal bed monitoring wells maintained by the Montana Bureau of Mines and Geology (MBMG), 4 coal bed monitoring wells installed by the United States Geological Survey (USGS) (Barnhart et al., 2016), and 5 coalbed methane (CBM) production wells in the northwestern portion of the PRB. All wells sampled as part of this study were completed and screened in individual coal seams.

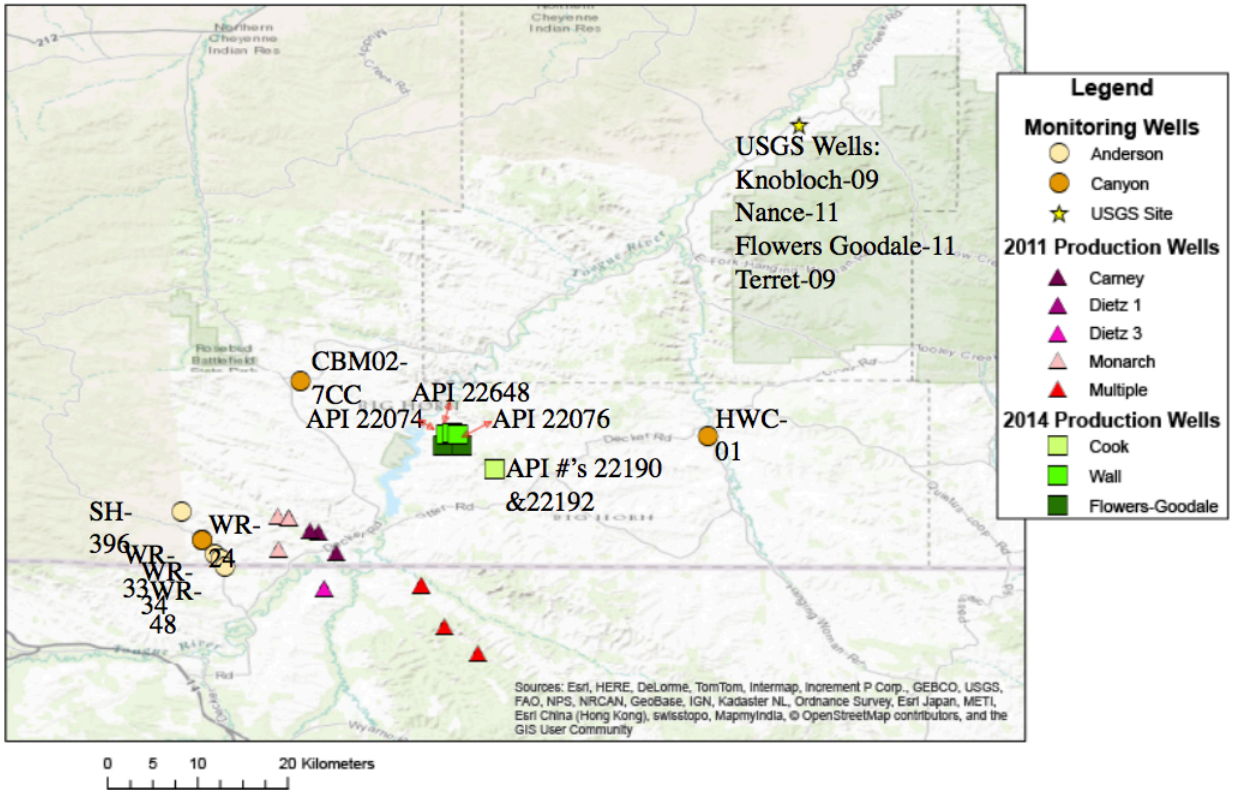

Figure 2. Location map of wells sampled as part of this study.

4.1 Sampling Strategy and Collection

Samples were collected across this range of coal seams and depths in order to reflect the variability of the water and gas chemistry of the fluids to determine their residence time and the potential microbiology of the coal seams as the coals differ laterally and with depth. Field notes were recorded at each sampled well and well name, API number, date, time, latitude and longitudinal coordinates were noted. Groundwater samples were collected after at least three well volumes had been purged from the wells. All water samples were filtered through a 0.45 µm pore-size syringe tip nylon filter and kept in coolers under ice to maintain a temperature of <4°C until analysis at the lab. Glass scintillation vials were used to collect samples for water stable isotopes

(δ^2H and $\delta^{18}O$). Tritium samples were collected, unfiltered, in 1 L HDPE bottles and $^{87}Sr/^{86}Sr$ samples were collected in 30 mL acid washed HDPE bottles (Ritter et al., 2015).

Groundwater samples for major gas abundance (CH_4, C_2H_6, N_2, O_2) and noble gas composition (He, Ne, Ar, and their isotopes) were collected directly from monitoring and CBM production wells (Darrah et al., 2013; 2015). Each well sample and duplicate was collected using copper tubing that had been cut to approximately 18 inches and attached inline to natural-gas wells. After 50 volumes of gas or water flowed through the copper tubing, the gas sample was trapped by cold-welding the copper using brass clamps (Darrah et al., 2015). Samples were stored at room temperature until they were shipped back to the lab to undergo natural gas molecular and isotopic analysis, including noble gas isotope geochemistry.

4.2 Analysis

For noble gas and major gas compositional analysis, each sample contained in the copper tubes was connected to a high vacuum processing line following standard methods (Darrah et al., 2015). Major gas components (e.g., N_2, O_2, Ar, CH_4, C_2H_6) were measured using an SRS quadrupole mass spectrometer (MS) and an SRI gas chromatograph (GC) (Darrah et al., 2013; Hunt et al., 2012). Before noble gas analysis, hydrocarbons and other impurities were removed to prevent isobaric interferences. This was achieved by successively exposing the gas sample to a heated Zirconium-Aluminum getter to remove nitrogen compounds and CO_2, a SAES getter to remove Hydrogen, followed by using a charcoal finger cooled to -95^oC using liquid nitrogen (LN_2) to isolate He and Ne from Ar, Kr, Xe, and finally an ARS cold head to separate He from Ne (Darrah et al., 2015).

After this process was completed, a small amount of helium was pipetted into the Thermo Fisher Helix SFT noble gas MS at Ohio State University and analyzed by standard methods (e.g.,

Darrah and Poreda, 2012). Each noble gas element was sequentially released from the ARS cold head by increasing the temperature. Following the sequential analysis of each noble gas, the results were compared.

Standard analytical errors were ±3% for noble gas concentrations ([^{4}He], [^{22}Ne], [^{40}Ar]). Isotopic errors were approximately ±0.01 times the ratio of air (or 1.4 x10^{-8}) for ^{3}He/^{4}He ratio, <±0.5% and <±1% for ^{20}Ne/^{22}Ne and ^{21}Ne/^{22}Ne, respectively, and <±1% for ^{38}Ar/^{36}Ar and ^{40}Ar/^{36}Ar, respectively (higher than normal because of interferences from C_3 on mass=36).

To evaluate the potential for *in-situ* radiogenic production and/or release of ^{4}He, U and Th were analyzed in samples collected from each of the coal seams. Analyses were conducted by standard methods using inductively coupled plasma mass spectrometry (ICP-MS) (Cuoco et al., 2013; Darrah et al., 2009). Diffusional rates for He, Ne, and Ar from each coal seam was determined by step-wise heating to produce an Arrhenius diffusion curve following Hunt (2000). Temperature was measured with 2 external thermocouples at the top and bottom of the chamber and maintained using a variable transformer. The average temperature between the two thermocouples was used, with an assigned temperature error of ±5^{o}C. Incremental helium measurements were made on a Thermo Fisher Helix SFT noble gas mass spectrometer by peak height comparison to a calibrated air standard with an error of <3%. Samples were heated to 30^{o}C, 50^{o}C, 100^{o}C, 200^{o}C, 300^{o}C, 400^{o}C, and 500^{o}C.

5. Results

The ^{4}He production from radioactive decay can be quantified and anticipated according to the U and Th content of the sediments (Kipfer et al., 2002). Coal seam solids and sandstone samples were gathered and analyzed for ^{4}He and $^{21}Ne_{excess}$ (i.e., $^{21}Ne^{*}$) concentrations after being collected directly from outcrops and core throughout the PRB.

Because ^{4}He diffusion through the coal seams occurs quickly on geological time scales (~10,000 years), in these slow-flowing CBM aquifers ^{4}He is expected to reach a steady-state where it is released from mineral grains and diffused into the groundwater as quickly as it is produced (Torgersen, 1980). With the assumption that this is true in shallow aquifers, it is possible to use the estimated transfer rates to determine the mean residence times of groundwater. The largest source of error in this calculation is the rate of diffusional ^{4}He loss from aquifer solids to the surrounded pore waters. If this can be accurately determined, mean residence time estimates can be estimated for various lithological units. The ^{4}He diffusion rates are reasonably well constrained for quartz and other siliclastic aquifers. Nonetheless, this fundamental work has not been done on coal seam solids to our knowledge. In the absence of empirical data, most workers assume steady-state production, which neglects the potential presence of excess ^{4}He in aquifers mineral grains.

The ^{4}He concentrations in the majority of samples significantly exceeded the anticipated helium contents for the measured U and Th concentrations even if one assumed in-growth times longer than the burial of the basin (Table 1). These results require that one empirically determine the transfer coefficients for ^{4}He from aquifer solids to pore waters. An excess of ^{4}He is indicative that there is some excess helium retained within the aquifer solids. The source is uncertain, but probably attributable to either being accumulated prior to sediment deposition (detrital) or as a result

of the dissolution of ^{4}He into grains during previous generations of ^{4}He-rich crustal fluid migration (Dowling et al., 2003; Carey et al., 2004; Darrah et al., 2015).

Table 1. PRB solid coal samples analyzed and the resulting measured ^{4}He content.

Sample	U	Th	Measured ^{4}He	Assuming 60 Million Years	Percent Lost
	(ppm)	(ppm)	µcc/kg	µcc/kg	%
Knobloch-1 Outcrop	2.416	5.465	9451.1	31800.0	0.70
Knobloch-2	1.987	4.984	19684.1	31800.0	0.38
Knobloch-3	2.467	4.845	23068.0	31800.0	0.27
Goodale-1	1.836	3.987	16938.5	31800.0	0.47
Goodale-2	1.924	6.021	9847.1	31800.0	0.69
Goodale-3	1.861	6.014	13120.1	31800.0	0.59
Goodale-4	2.015	5.154	11654.1	31800.0	0.63
Goodale-5	2.358	5.311	31446.6	31800.0	0.01
Flowers-1	2.514	5.014	18754.6	31800.0	0.41

In the Noble Gas Laboratory at The Ohio State University, diffusional release of ^{4}He from coal seam solid samples was measured using a stepwise heating experiment. Release estimates have been corrected for air contamination by assuming that all ^{3}He is purely atmospheric resulting from leakage of air into the vacuum line or air trapped in the sample itself. The ^{4}H release rates of the three coal samples with increasing temperature are linear through ~200^{o}C and all produce similar slopes on the Arrhenius plots (Table 2). This observation indicates similar diffusion coefficients over the temperature interval of at least 22–200^{o}C throughout the three samples from different coal seams.

The ^{4}He release rates are calculated using the Arrhenius curves and the data from Table 1. These ^{4}He values range from 442 to 491 µcc/kg/yr across the three coal seams sampled from the

PRB (Table 2). As illustrated, these rates of ^{4}He production are ~800 times greater than typical production rates from sandstone and carbonate aquifers, which are ~0.5 ± 0.15 µcc/kg/yr (Hunt, 2000; Dowling et al., 2003; Carey et al., 2003). These results suggest that at least over short periods of time, steady-state and standard models of ^{4}He release may dramatically overestimate the true mean residence time of groundwater in coal seams.

Table 2. Step-wise heating of three different coal solid samples and their measured ^{4}He content.

Step-wise Heating	Knobloch-1	Goodale-1	Flowers-1
1 hour increments (Deg C)	Measured ^{4}He (µcc/kg)		
50.0	21.7	30.3	31.6
100.0	888.0	917.7	3354.6
200.0	14265.4	11657.9	10245.6
300.0	4016.6	3215.9	3796.4
400.0	412.2	1072.6	699.7
500.0	80.2	44.2	626.7
Cumulative	**19684.1**	**16938.5**	**18754.6**

6. Discussion

Before groundwater residence times can be calculated from the release of ^{4}He, exogenous sources of crustal helium and two-phase effects need to be identified in order to understand the potential for artificially inflated ^{4}He concentrations. If these components can be accounted for, the residual ^{4}He concentrations (termed excess radiogenic ^{4}He) can then be used to estimate the amount of ^{4}He that accumulated from either the release from detrital grains or the production from U and Th. Once the release rate of ^{4}He from detrital grains can be measured empirically, the excess

Table 3. Helium concentrations of groundwater from sampled coal beds.

	^{4}He
Sample	**µcc/L**
MW-1 WR48 (Redo)	492
MW-2 WR33	110
MW-3 WR24	881
MW-4 HWC-01A (antelope)	52402
MW-5 CBM02-7CCA	1014
MW-6 SH-396A	545
MW-7 WR34 A	862
USGS K-09	6150
USGS F-11	95418
USGS T-09	59005
USGS N-11	17788
API22074 water	179
API22190 water	2710
API22192 water	19580
API22648 water	876
API22706 water	791

radiogenic ^{4}He can then be used to calculate the residence time that has elapsed since groundwater has recharged.

Helium concentrations of groundwater in the sampled coal beds range from 110 µcc/L to 9.5 x10^{4} µcc/L (Table 3). This lends credence to the hypothesis that excess ^{4}He in the groundwater is radiogenic in origin, rather than the result of a mantle-derived source (Holland et al., 2013). Residence times of groundwater are typically calculated using a model which assumes 30% porosity, measured quartz diffusion coefficients, and a 1-D radial diffusion model (Fetter, 2001).

Herein, we assumed that the maximum diffusion rate from shallow aquifers of 0.5x10^{-6} STP/L/yr in siliclastic lithologies was appropriate and calculated the residence times accordingly (Ritter et al.,, 2015). This model produced results ranging from a residence time of ~130 years at well WR-33, to 191,000 years at USGS well MT-2FG-11 (Table 4). However, it is important to note a residence time calculation is only appropriate for steady state situations when the groundwater in question is flowing through a lithological unit with the same rate of ^{4}He release as assumed here (i.e., this model uses the release rate for a sandstone aquifer for the majority of its residence time). Therefore, these results necessitate the need to constrain new residence times according to a model that assumes the groundwater is flowing through the coal seams for the majority of its residence time.

With the measured diffusional release rates of helium from coal seams in the PRB of 119x10^{-6} STP/L/yr, the model produces results yielding unrealistically low residence times ranging from of ~4 to 800 years (Table 4) when the model is considering the coal-only residence times.

Thus, even if our previous groundwater estimates were inflated, based on considering only the coal-seam aquifer model one would conclude that the groundwater in the PRB must have spent the majority of its residence time in a sandstone aquifer and mixed (or came in contact) with fluids

in coal seams in the recent geological past. For these reasons, I infer that there is communication in groundwater between the coal seams and overlying sandstones in this basin, which leads to the water having short, intermittent contact with coal seams while spending the majority of the time flowing through the sandstone aquifers.

Table 4. Comparison of calculated residence times using the standard diffusion rate of $0.5x10^{-6}$ STP/L/yr, versus the coal-only diffusion rate of $119x10^{-6}$ STP/L/yr (Ritter et al., 2015).

Well Name	Tritium		^4He	^{20}Ne	^{36}Ar	^{84}Kr	R/R_a	Residence Time	
	(T.U.)	Error	10^{-5} cm^3 STP/L					(Years)	
CBM Production Wells								*Standard Model*	*Coal Diffusion Model*
Visborg 13W-17-08-41	<0.8		178.8	389.2	1550.0	66.8	0.513	2.7E+02	1.5E+00
Visborg 14WP-17-08-41	0.7	0.31	875.5	234.9	954.9	38.3	0.135	1.7E+03	7.4E+00
Visborg 15W-17-08-41	1.0	0.38	791.3	309.6	1026.6	39.0	0.201	1.5E+03	6.6E+00
Rancholme 03CA-34-08-41	2.0	0.40	19579.9	330.8	1044.5	71.9	0.024	3.9E+04	1.6E+02
Rancholme 03CC-34-08-41	<1.0		2710.2	251.4	956.2	34.3	0.057	5.3E+03	2.3E+01
Monitoring Wells (Montana Bureau of Mines and Geology)									
SH-396			544.6	254.3	1307.0	89.6	0.244	1.0E+03	4.6E+00
WR-33	9.4	0.48	110.1	257.1	1516.3	7.1	1.204	1.3E+02	9.3E-01
WR-34			862.4	189.1	1220.5	96.3	0.078	1.6E+03	7.2E+00
WR-48	0.6	0.29	491.9	221.9	1247.3	45.5	0.356	8.9E+02	4.1E+00
WR-24			880.6	298.0	1235.7	95.1	0.162	1.7E+03	7.4E+00
CBM02-7cc			1014.1	245.2	1356.5	101.2	0.116	1.9E+03	8.5E+00
HWC-01			52401.5	156.2	553.5	35.1	0.012	1.0E+05	4.4E+02
Monitoring Wells (U.S. Geological Survey)									
MT-2K-09	<0.5		6149.7	264.0	1225.6	34.4	0.028	1.2E+04	5.2E+01
MT-2N-11	0.8	0.26	17788.3	223.3	1160.1	46.9	0.024	3.5E+04	1.5E+02
MT-2FG-11	<0.9		95417.5	124.7	996.9	21.9	0.013	1.9E+05	8.0E+02
MT-2T-09	<1.0		59004.9	132.0	1104.2	33.6	0.013	1.2E+05	5.0E+02

The relationship between groundwater residence times and empirically determined release of ^{4}He from the two different lithological sources (sandstone and coal seam solids) was tested for three different scenarios. For each scenario, it was assumed that some ^{4}He diffused from sandstone aquifers according to the standard He release model, while the remaining He is from coal. The three scenarios analyzed were: 90% of He from sandstone/10% from coal, 50% of He from sandstone/50% from coal, and 10% of He from sandstone/90% from coal.

Apparent residence times were calculated for the sandstone and coal seam solid portions of ^{4}He separately and then added to produce a total estimated residence time (Table 5). The sensitivity analysis implies that groundwater contact time with the coals is apparently less than adjacent sandstones, regardless of the amount of He diffusion from each source. Even in the 10% sandstone/90% coal scenario, contact time with coal still accounts for <10% of the total residence time of water, but a significant proportion of the total ^{4}He. While it was thought that PRB coals are the primary water-producing formations in the basin due to their highly fractured and permeable nature (Wheaton and Metesh, 2002), these results tell us that the sandstone formations have the largest impact on the groundwater flow in and out of the basin and possibly contribute the most to the recharge of the area.

Table 5. Sensitivity analysis of residence times (R.T.) using three different scenarios for diffusion rates of ^{4}He from sandstone and coal (Ritter et al., 2015).

Well Name	90% Sandstone/10% Coal				50% Sandstone/50% Coal				10% Sandstone/90% Coal			
	SS R.T. (years)	*Coal R.T. (years)*	*Total R.T. (years)*	*%of time in coal*	*SS R.T. (years)*	*Coal R.T. (years)*	*Total R.T. (years)*	*%of time in coal*	*SS R.T. (years)*	*Coal R.T. (years)*	*Total R.T. (years)*	*%of time in coal*
CBM Production Wells												
Visborg 13W-17-08-41	2.30E+02	1.50E-01	2.30E+02	0.06	8.90E+01	7.50E-01	9.00E+01	0.84	0.0E+00*	1.40E+00	*	*
Visborg 14WP-17-08-41	1.50E+03	7.40E-01	1.50E+03	0.05	7.90E+02	3.70E+00	7.90E+02	0.47	8.50E+01	6.60E+00	9.20E+01	7.22
Visborg 15W-17-08-41	1.30E+03	6.60E-01	1.30E+03	0.05	7.00E+02	3.30E+00	7.00E+02	0.47	6.80E+01	6.00E+00	7.40E+01	8.06
Rancholme 03CA-34-08-41	3.50E+04	1.60E+01	3.50E+04	0.05	1.90E+04	8.20E+01	2.00E+04	0.42	3.80E+03	1.50E+02	4.00E+03	3.73
Rancholme 03CC-34-08-41	4.80E+03	2.30E+00	4.80E+03	0.05	2.60E+03	1.10E+01	2.60E+03	0.43	4.50E+02	2.00E+01	4.70E+02	4.34
Monitoring Wells (Montana Bureau of Mines and Geology)												
SH-396	8.90E+02	4.60E-01	8.90E+02	0.05	4.50E+02	2.30E+00	4.60E+02	0.5	1.90E+01	4.10E+00	2.30E+01	17.88
WR-33	1.10E+02	9.30E-02	1.10E+02	0.09	2.00E+01	4.60E-01	2.10E+01	2.25	0.0E+00*	8.30E-01	*	*
WR-34	1.50E+03	7.20E-01	1.50E+03	0.05	7.70E+02	3.60E+00	7.80E+02	0.47	8.20E+01	6.50E+00	8.90E+01	7.33
WR-48	8.00E+02	4.10E-01	8.00E+02	0.05	4.00E+02	2.10E+00	4.00E+02	0.51	8.40E+00	3.70E+00	1.20E+01	30.73
WR-24	1.50E+03	7.40E-01	1.50E+03	0.05	7.90E+02	3.70E+00	7.90E+02	0.47	8.60E+01	6.70E+00	9.30E+01	7.18
CBM02-7cc	1.70E+03	8.50E-01	1.70E+03	0.05	9.20E+02	4.30E+00	9.30E+02	0.46	1.10E+02	7.70E+00	1.20E+02	6.37
HWC-01	9.40E+04	4.40E+01	9.40E+04	0.05	5.20E+04	2.20E+02	5.30E+04	0.42	1.00E+04	4.00E+02	1.10E+04	3.67
Monitoring Wells (U.S. Geological Survey)												
MT-2K-09	1.10E+04	5.20E+00	1.10E+04	0.05	5.10E+03	2.60E+01	5.10E+03	0.42	1.10E+03	4.70E+01	1.20E+03	3.92
MT-2N-11	3.20E+04	1.50E+01	3.20E+04	0.05	1.80E+04	7.50E+01	1.80E+04	0.42	3.50E+03	1.30E+02	3.60E+03	3.73
MT-2FG-11	1.70E+05	8.00E+01	1.70E+05	0.05	9.50E+04	4.00E+02	9.60E+04	0.42	1.90E+04	7.20E+02	2.00E+04	3.66
MT-2T-09	1.10E+05	5.00E+01	1.10E+05	0.05	5.90E+04	2.50E+02	5.90E+04	0.42	1.20E+04	4.50E+02	1.20E+04	3.67

This ad hoc hypothesis generated from the helium release data is also supported by strontium isotope data. Groundwater flow throughout the sandstone and coal of the PRB was further illustrated using radiogenic ($^{87}Sr/^{86}Sr$) isotope tracers with the noble gas data. There is a high degree of variance in strontium isotope ratios detected in the groundwater, from ~0.7085 to ~0.7130. Strontium isotope ratios of groundwater in the Tongue River watershed were measured in another study and showed similar isotopic ratios, indicating that groundwater in the area interacted with both sandstone and coal units (Pearson, 2002; Campbell et al., 2008). These similar ratios leads to the assumption that there would be residence within both units as the fluids evolved. These results support the hypothesis generated from the He analysis, which suggested that groundwater in the Tongue River watershed spends most of its time in contact with sandstone and is later transmitted to the coal seams, even potentially following drawdown. In addition, strontium isotope ratios tend to vary widely at short residence times, while long residence time values seem to stabilize between 0.7085 and 0.7090. Previous studies have suggested that lower values reflect more influence from sandstone (Pearson, 2002; Campbell et al., 2008). This leads me to believe that the groundwater with longer residence times most likely spends more time flowing through sandstone units.

7. Conclusions

Noble gas isotopes are ideal tracers for use in determining the residence time and flow path of groundwater. In this study, the rate of production and subsequent diffusion of helium throughout the coal and sandstone units of the Powder River Basin was quantified. This helped to evaluate the apparent residence times in various formations and constrain the flowpaths of the groundwater and rates and locations of aquifer recharge. Surprisingly, this study reveals that the water in the Powder River Basin is recharged much more frequently than originally suspected as the oldest calculated residence time was still <200,000 years. The diffusional release of ^{4}He from coal solid samples was measured in a stepwise heating experiment. This produced results showing rates of ^{4}He production ~800 times greater than typical production rates from sandstone and carbonate aquifers. However, this is far too high a rate for the groundwater to be in contact with the coal seams for the majority of its lifetime. Furthermore, calculated residence times using a coal-only model produce unrealistically low values ranging from ~4 years to 800 years. This, compared to the sandstone aquifer model which gave us estimated residence times ranging from ~130 years to nearly 200,000 years, provides additional evidence for the hypothesis that mixing of groundwater is occurring in the PRB and that the sandstone is the primary water producing aquifer of the basin.

Despite previously held assumptions, the study finds that the coal seams of the PRB are likely not the primary water-producing unit and that instead the groundwater spends the majority of its time in sandstone. This is further supported by the radiogenic $^{87}Sr/^{86}Sr$ isotope tracers data, which yielded a similar isotopic ratio as results from a previous study in the Tongue River watershed, a mixed influence of sandstone and coal units on the groundwater's chemistry. This research highlights how useful of a hydrogeological tool quantifying residence times can be not only for water quality, but industrial applications as well. These results and data from similar

studies can be used to understand recharge location and timing which then can be extrapolated to create models for dewatering aquifers in the search of and production of CBM. With further research, this can give us a better understanding of the conditions under which we can operate to avoid excessive depletion of the water table, the negative impact it would have on agricultural systems, and how to combat the potentially adverse effects on drinking water quality for municipalities.

8. Suggestions For Future Research

Further research into the specifics of water transport through different lithological units would be helpful in properly constraining residence times using noble gases. This study provided valuable insight into the flowpaths of groundwater through coal seams. However, it left even more questions unanswered as it did not determine specific constraints of water transport through more unique aquifer systems. Furthermore, this technique is applicable to other coal-bed basin systems and could be extrapolated for use in similar geologic settings to better understand how coalbed methane production affects the groundwater residence times and recharge rates.

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